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COATING MATERIAL FOR FORMING TRANSPARENT PHOTOCATALYTIC DISPERSION FILM AND METALLIC PLATE COATED WITH TRANSPARENT PHOTOCATLYTIC DISPERSION FILM

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Abstract of **JP 2001323188 (A)**

PROBLEM TO BE SOLVED: To provide a coating material capable of improving the stability of the coating material in which particles of a photocatalyst are suspended and suited in forming a transparent photocatalytic dispersion film, and a coated steel plate which retains excellent hydrophilicity over a long period of time. **SOLUTION:** The coating material is composed of a boehmite sol, crystalline photocatalyst particles

or a precursor which comes to crystalline photocatalyst particles after heat treatment, and a mixed solvent of water and an organic solvent with a mass ratio of the crystalline photocatalyst particles after heat treatment to the boehmite and/or γ -alumina in the range of 10:90 to 60:40 and a mass ratio of the water in the mixed solvent to the organic solvent in the range of 90:10 to 40:60 after heat treatment. Based on the crystalline photocatalyst particles after heat treatment, 10-50 pts. mass silane coupling agent can be incorporated. As the silane coupling agent, an epoxy based or methacryloxy based silane coupling agent is used. As the organic solvent, one or more kinds selected from alcohols, ethers, and ketones are used and of them, at least one kind preferably has a boiling point higher than that of water.

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Family list**1 application(s) for: JP2001323188 (A)**

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**COATING MATERIAL FOR FORMING
TRANSPARENT PHOTOCATALYTIC****1 DISPERSION FILM AND METALLIC PLATE
COATED WITH TRANSPARENT
PHOTOCATLYTIC DISPERSION FILM****Inventor:** ANDO AKIHIRO ; KOURA
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METHOD OF PRODUCING BOEHMITE SOL, BOEHMITE SOL, METHOD OF PRODUCING RECORDING MEDIUM AND RECORDING MEDIUM

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NOTICES *

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

[Claim(s)]

[Claim 1] boehmite -- it consisting of a partially aromatic solvent of a precursor and a water-organic solvent used as crystalline photocatalyst grains, and after sol, crystalline photocatalyst grains, or heat treatment, a mass ratio with crystalline photocatalyst grains after heat treatment, boehmite, and/or gamma alumina serves as the range of 10:90-60:40 -- as -- crystalline photocatalyst grains and boehmite -- sol being blended and, A paint for transparent photocatalyst distribution coat formation, wherein a mass ratio of water of a partially aromatic solvent and an organic solvent is adjusted to the range of 90:10-40:60.

[Claim 2] The paint for transparent photocatalyst distribution coat formation according to claim 1 which contains an epoxy system or a methacryloxy-system silane coupling agent of ten to 50 mass part to crystalline photocatalyst grains after heat treatment.

[Claim 3] The paint for transparent photocatalyst distribution coat formation according to claim 1 which is one sort as which an organic solvent was chosen from alcohols, ether, and ketone, or two sorts or more, and has before long the boiling point when at least one sort is higher than water.

[Claim 4] A coated metal plate in which a transparent photocatalyst distribution coat, wherein a coat in which a mass ratio with crystalline photocatalyst grains, boehmite, and/or

gamma alumina has the presentation of 10:90-40:60 is formed in a metal plate surface was formed.

[Claim 5] Crystalline photocatalyst grains : that a coat in which the remainder has the presentation of boehmite and/or gamma alumina in ten to 60 mass %, 0.1 to silica:10 mass [of silane coupling agent origin] %, and below organic functional group:5 mass % of silane coupling agent origin is formed in a metal plate surface. A coated metal plate in which a transparent photocatalyst distribution coat by which it is characterized was formed.

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention can form the photocatalyst distribution coat which presents the hydrophilic nature outstanding from the time of membrane formation, and relates to the coated metal plate covered with the transparent photocatalyst distribution coat formed from the paint excellent also in storage stability, and this paint.

[0002]

[Description of the Prior Art] The method of fixing a photocatalyst is adopted as immobilization of a photocatalyst by applying the paint containing a photocatalyst to the surfaces, such as a metal base, baking it, and drying.

Silica (PCT/JP96/00733), formless alumina (JP,H9-227805,A), etc. are used as a binder.

According to these methods, the coat which presents the outstanding hydrophilic nature of ten opposite water contact angles or less is obtained, and the hydrophilic nature which was excellent as long as the photocatalyst was moreover excited by the optical exposure is maintained. If the very small photocatalyst grains of particle diameter are made to bind with a transparent binder, a transparent photocatalyst thin film with high visible light transmittance will be formed.

[0003] However, in the photocatalyst distribution coat which uses silica as a binder, hydrophilic nature is not shown, but hydrophilization is begun and carried out by optical exposure

at the beginning of membrane formation. If binding energy (101.5 kcal/(mol)) uses the Si-O combination in a silica binder where a photocatalyst is excited for a long time since it is small as compared with the binding energy (136 kcal/(mol)) of aluminum-O combination, Si-O combination will be easy to be cut. Cutting of Si-O combination becomes causes, such as a crack generation of a coat, a coat white blush mark, coat exfoliation, and a transparency fall. Even when using formless alumina for a binder, if you have no optical exposure like silica, hydrophilization is not carried out, and since water storability is low as compared with silica, moreover, good hydrophilic nature cannot be maintained over a long period of time. In formless alumina, if long term use is carried out, partial crystallization etc. will arise from an amorphous state, a coat milks, and transparency falls easily.

[0004] On the other hand, this invention persons proposed the transparent photocatalyst distribution coat which uses boehmite and/or gamma alumina as a binder by Tokuganhei11-246873. Since crystalline boehmite is used for a raw material, an organic component is hardly contained in a coat, Boehmite and/or gamma alumina with the OH radical of hydrophilic nature serve as a binder, the hydrophilic nature of ten opposite water contact angles or less is presented from the time of membrane formation, the durability of hydrophilic nature is also good and the photocatalyst distribution coat excellent also in adhesion or weatherability is formed.

[0005]

[Problem(s) to be Solved by the Invention] however -- using water for a solvent -- boehmite -- in the paint which distributed sol, crystalline photocatalyst grains, or a photocatalyst-grains precursor, at the time of storage, it condenses, or is easy to gel, and inferior to storage stability. Also at the time of calcination, if rapid heating is carried out, a coat will bloom and adhesion will fall easily. Therefore, film adhesion needed to make the good transparent photocatalyst distribution coat form by prolonged calcination for 20 minutes or more at the

temperature of not less than 200 **, and a photocatalyst distribution coat with film adhesion sufficient in short-time calcination, transparency, and weatherability for 5 or less minutes was not able to be formed.

[0006] This invention is thought out that such a problem should be solved and is a thing.

The purpose is excellent in storage stability by using the partially aromatic solvent of a water-organic solvent, Hydrophilic nature and transparency are high and it is providing the coated metal plate covered with the transparent photocatalyst distribution coat which maintains good hydrophilic nature over the paint for transparent photocatalyst distribution coat formation and long period of time which can form the photocatalyst distribution coat excellent also in film adhesion or weatherability.

[0007]

[Means for Solving the Problem] In order that a paint for transparent photocatalyst distribution coat formation of this invention may attain the purpose, boehmite -- it consisting of a partially aromatic solvent of a precursor and a water-organic solvent used as crystalline photocatalyst grains, and after sol, crystalline photocatalyst grains, or heat treatment, a mass ratio with crystalline photocatalyst grains after heat treatment, boehmite, and/or gamma alumina serves as the range of 10:90-60:40 -- as -- crystalline photocatalyst grains and boehmite -- sol being blended and, A mass ratio of water of a partially aromatic solvent and an organic solvent is adjusted to the range of 90:10-40:60.

[0008] This paint for transparent photocatalyst distribution coat formation can contain a silane coupling agent of ten to 50 mass part to crystalline photocatalyst grains after heat treatment. A silane coupling agent of an epoxy system or a methacryloxy-system is used for a silane coupling agent. As an organic solvent, one sort chosen from alcohols, ether, and ketone or two sorts or more are used, and, as for at least one

sort, it is preferred to have the boiling point higher than water before long.

[0009] As for a coated metal plate covered with a transparent photocatalyst distribution coat, a coat whose mass ratio with crystalline photocatalyst grains, boehmite, and/or gamma alumina has the presentation of 10:90-40:60 is formed in a metal plate surface. In a coat formed from a paint which contains a silane coupling agent in a paint. Crystalline photocatalyst grains: In ten to 60 mass %, 0.1 to silica:10 mass [of silane coupling agent origin] %, and below organic functional group:5 mass % of silane coupling agent origin, the remainder has the presentation of boehmite and/or gamma alumina.

[0010]

[Function] boehmite -- the paint which made water distribute sol and crystalline photocatalyst grains, or a crystalline photocatalyst-grains precursor has bad storage stability, a coat blooms by the rapid heating at the time of calcination, and adhesion falls. This invention persons thought that these faults had a cause in solvent balance. namely, the boehmite which is a formed element (formed element after coat formation) in a paint -- sol and crystalline photocatalyst grains, or a crystalline photocatalyst-grains precursor, If all are independent, water dispersibility is good, but if mixture dispersion is carried out, it will be easy to produce partial dehydration condensation and condensation between heterogeneity, and a dispersibility fall in an aquosity solvent and by extension, storage stability will fall.

[0011] then -- using the partially aromatic solvent of water and a water soluble organic solvent -- boehmite -- when sol and crystalline photocatalyst grains, or a crystalline photocatalyst-grains precursor was distributed, it found out that the storage stability of a paint improved. this -- boehmite -- the partial solvation of sol, crystalline photocatalyst grains, or the crystalline photocatalyst-grains precursor is carried out to an organic solvent, and it is thought that it is because the stable dispersion to the inside of a paint became

possible. The effect which combination of an organic solvent exerts on storage stability becomes remarkable by solvent composition ratio above 10 mass %. since [however,] the solvation of the formed element in a paint is carried out thoroughly and hydrophobicity increases in the solvent which blended an excessive amount of organic solvents exceeding 60 mass % -- on the contrary -- condensation -- it becomes easy to gel.

[0012]Also when the partially aromatic solvent of a water-organic solvent prevents a coat from blooming at the time of calcination, it is effective. It is thought that it is because several solvents in which the boiling points differ volatilize in each boiling point that a partially aromatic solvent is effective in control of blooming. Especially, it becomes much more advantageous to an elevated temperature and short-time calcination, without blooming and adhesion reduction of a coat arising, even if it carries out rapid heating to a higher temperature if an organic solvent with the boiling point higher than water is blended as at least one ingredient. On the other hand, if a water simple substance is used as a solvent, a solvent will volatilize at a stretch in 100 ** of boiling points of water, and when a coat porosity-izes easily, blooming will advance.

[0013]The photocatalyst distribution coat which consists of crystalline photocatalyst grains and boehmite, and/or gamma alumina is excellent in weatherability, and even when he has no UV irradiation, it shows the hydrophilic nature outstanding from the time of membrane formation. However, prolonged calcination is needed in order to obtain film adhesion and weatherability sufficient in usual. In this point and this invention, by adding a silane coupling agent if needed under the conditions which control the fall of the hydrophilic nature by an organic component being introduced into a coat, and weatherability, bridge construction / hardening reaction is promoted and formation of the transparent photocatalyst distribution coat which has necessary strength by short-time calcination is enabled.

[0014]

[Embodiment of the Invention] the boehmite which made the partially aromatic solvent of the water-organic solvent distribute the precursor which serves as crystalline photocatalyst grains after crystalline photocatalyst grains or heat treatment so that a mass ratio with the crystalline photocatalyst grains after heat treatment, boehmite, and/or gamma alumina may be set to 10:90-60:40 -- sol is blended. The boehmite and/or gamma alumina with the OH radical of hydrophilic nature show the hydrophilic nature outstanding from the time of membrane formation, and generate a coat also with the good durability of hydrophilic nature. The crystal of boehmite and/or gamma alumina with a big aluminum-O combination of binding energy has a strong resistance force to cutting of aluminum-O combination, and unlike formless alumina, since it is already a crystallized state, it does not produce a crystallizing reaction, either. Therefore, the crack generation and coat white blush mark of a coat are controlled.

[0015] Crystalline photocatalyst grains present the hydrophilic nature in which itself was excellent by being excited by optical exposure, and in order to disassemble the organic matter dirt of a paint film surface, temporal degradation of the hydrophilic nature by dirt adhesion is controlled, and they make the hydrophilic nature outstanding over the long period of time maintain. As crystalline photocatalyst grains, although there are titanium oxide, a zinc oxide, strontium titanate, tungstic oxide, tin oxide, zirconium oxide, etc., use of big titanium oxide of chemical stability or photocatalyst activity is preferred. A photocatalyst effect when excited by optical exposure becomes remarkable with the loadings of ten or more mass parts, and crystalline photocatalyst grains recover the hydrophilic nature which originated in organic matter dirt and fell for a short time. However, combination of an excessive amount of crystalline photocatalyst grains exceeding 60 mass parts will reduce hydrophilic nature easily in a dark place without an optical

exposure for a short time.

[0016] As a raw material of crystalline photocatalyst grains, the precursor used as crystalline photocatalyst grains can also be used after heat treatment. There are metal hydroxide etc. which are produced by hydrolyzing various metal alkoxides and metal salt as such a precursor. for example, the case where titanium oxide is used as crystalline photocatalyst grains -- titanium tetraisopropoxide, titanium hydroxide, etc. -- boehmite -- it is added by sol. Titanium tetraisopropoxide and titanium hydroxide become an anatase type crystal which presents the outstanding photocatalyst activity, when heat-treating the paint applied to the metal plate surface at 400-600 **.

[0017] If a silane coupling agent is added in paints, bridge construction / hardening reaction of a coat will be promoted, and firing time will be shortened. However, there is a possibility that addition of a silane coupling agent may mean that an organic component is introduced into a coat, and hydrophilic nature may not be revealed at the time of membrane formation, and the organic component in a coat may be decomposed by the photocatalysis, and weatherability may fall. Then, when adding a silane coupling agent and carrying out short-time calcination, an addition is set up so that ten to 50 mass part may become comparatively to the crystalline photocatalyst grains after heat treatment. A silane coupling agent is an addition of ten or more mass parts, the effect that particle diameter promotes bridge construction / hardening reaction to the small big photocatalyst grains and boehmite, and/or gamma alumina of specific surface area becomes remarkable, and a coat with the adhesion and weatherability sufficient by short-time calcination for 5 or less minutes is formed. However, if an excessive amount of silane coupling agents exceeding 50 mass parts are added, the organic component contained in the generated coat increases, initial hydrophilicity falls, and it will originate in the numerical increase in Si-O combination, and weatherability will also fall.

[0018] The silane coupling agent is provided with the both sides of the OH radical by hydrolysis, and a polymerization nature organic functional group. Unless it has adverse effects, such as condensation and gelling, at the time of paint preparation, a kind is not restrained exceptionally, but when a polymerization nature organic functional group raises film adhesion, its methacryloxy-groups, such as epoxy groups, such as 3-glycidoxyl propyl group, and 3-methacryloxypropyl group, are preferred. Specifically,

3-glycidoxylpropyltrimetoxysilane,

3-glycidoxylpropylmethyldimetoxy silane, 3-methacryloxy propyl trimethoxysilane, 3-methacryloxy propyl methyl dimethoxysilane, etc. are mentioned.

[0019] The paint for transparent photocatalyst distribution coat formation according to this invention is specifically prepared as follows. making solvents, such as water or water / alcohol, distribute boehmite with a primary particle diameter of 20 nm or less -- boehmite -- considering it as sol -- this boehmite -- the suspension which made sol distribute crystalline photocatalyst grains with a primary particle diameter of 10 nm or less is prepared. In also making short-time calcination into an usable paint, it adds to suspension the silane coupling agent which promotes bridge construction and the effect reaction of a coat. the boehmite before adding a silane coupling agent beforehand to solvents, such as water or water / alcohol, or adding crystalline photocatalyst grains -- it may add to sol.

[0020] As a paint negative, various plating steel plates, a stainless steel plate, an aluminum plate, etc. are used. In order that a paint negative may improve film adhesion, pretreatment of degreasing, phosphate treating, chromate treatment, etc. is performed if needed. In advance of formation of a transparent photocatalyst distribution coat, a clear coat can be made into the 1st layer and it can also form in a metal plate surface. Since a clear coat has an OH radical in the surface, the chemical bond of it is firmly carried out to the transparent

photocatalyst distribution coat provided on it, and it raises the adhesion of a transparent photocatalyst distribution coat. As a clear coat, in order to suppress generating of an interference color, it is preferred to provide a transparent oxide coat with a low refractive index by the thickness of 1 micrometers or more of thickness. A transparent oxide coat is formed by applying to a metal plate the paint of the shape of sol which uses as a raw material the precursor which serves as an oxide, for example after oxides, such as alumina, silica, and zeolite, or heat treatment, and heat-treating it. At this time, a dehydrating condensation reaction is carried out to the OH radical of the metal plate surface where the OH radical contained in the sol of coating components was pretreated, and it becomes the clear coat firmly combined with the metal plate surface.

[0021] In forming a coat using the paint for transparent photocatalyst distribution coat formation which does not contain a silane coupling agent, after applying a paint, it heat-treats 20 minutes or more at 200-600 **. Bridge construction / hardening reaction of a coat progresses, and the coat of necessary strength is formed by this heat treatment. However, in the heat treatment temperature over 600 **, in order that the crystalline form of alumina may change and a surface OH radical may decrease, the tendency for the hydrophilic nature of a coat to fall is seen. In the paint which added the silane coupling agent, although the coat of necessary strength is formed by heat treatment for less than 5 minutes, it is required to set up heat treatment temperature and time so that the organic functional group which remains easily in a coat may decrease.

[0022] As for the paint adjusted to prescribed composition, ten to crystalline photocatalyst-grains:60 mass %, 0.1 to silica:10 mass [of silane coupling agent origin] %, and below organic functional group:5 mass % of silane coupling agent origin serve as a coat in which the remainder has the presentation of boehmite and/or gamma alumina after calcination. Since the organic functional group of silane coupling agent origin is regulated

below to 5 mass %, good initial hydrophilicity is revealed and the coat excellent in weatherability is formed. Since the silica of silane coupling agent origin is adjusted to the range of 0.1 - 10 mass %, the added silane coupling agent is enough used for bridge construction / hardening reaction of a coat, and the fall of the weatherability resulting from the increase in Si-O combination is also controlled.

[0023]

[Work example 1] The example 1 (example of this invention) of membrane formation

It rinsed and dried, after using the bright-annealing finishing material of the SUS304 stainless steel of 0.8 mm of board thickness for the paint negative and performing alkaline degreasing. a paint makes water and the partially aromatic solvent (water: butyl-cellosolve =70:30) of butyl cellosolve distribute boehmite -- boehmite -- it adjusted by considering it as sol and also distributing an anatase-type-titanium-oxide particle with a particle diameter of 7 nm. The paint was applied to the stainless steel plate and the transparent photocatalyst distribution coat was formed by the heating calcination for 300 **x 30 minutes.

[0024] The example 2 (example of this invention) of membrane formation

The paint which added the epoxy system silane coupling agent (3-glycidoxypolytrimetoxysilane) in the paints of the example 1 of membrane formation at a rate of 30 mass parts to titanium oxide was used. This paint was applied to the stainless steel plate, and the transparent photocatalyst distribution coat was formed by the heating calcination for 300 **x 5 minutes.

The example 3 (example of this invention) of membrane formation It changed to anatase type titanium oxide, titanium

tetraisopropoxide was dissolved in isopropanol, and the titanium oxide precursor which added diisopropanolamine was used. And the paint was prepared by the same method as the example 2 of membrane formation, and the transparent photocatalyst distribution coat was formed by the heating calcination for 450

**x 5 minutes.

[0025] The example 4 (comparative example) of membrane formation
The coat was formed like the example 1 of membrane formation
except using the mixed solvent which set the mass ratio of water
and butyl cellosolve to 95:5 and 30:70.

The example 5 (comparative example) of membrane formation
The coat was formed like the example 2 of membrane formation
except using the paint which added the epoxy system silane
coupling agent at a rate of five mass parts and 70 mass parts
with the mass ratio to titanium oxide.

The example 6 (comparative example) of membrane formation
The coat was formed like the example 2 of membrane formation
except using the paint which added the amino ** silane coupling
agent (N-(2 **AMINO ethyl) 3 **AMINO propyltrimethoxysilane).

[0026] The storage stability of a paint and the physical
properties of a coated steel sheet which were prepared in each
example of membrane formation were investigated by the
following method.

After keeping the paint in which the paint carried out storage
stability preparation for one month in ordinary temperature
atmosphere, the dispersion state of the paint was observed and
the existence of condensation or gelling and viscosity change
were investigated.

It is immediately after initial hydrophilicity membrane
formation of a coated steel sheet, waterdrop was dropped at the
coat before UV irradiation, the angle of the side which contains
waterdrop among the angles between the tangent and film surface
which were lengthened for waterdrop in the point of contact of
the three phase circuit of a coat, waterdrop, and air was
measured as an opposite water contact angle, and this measured
value estimated initial hydrophilicity.

[0027] After carrying out hydrophilization of the coat by the
ultraviolet ray intensity in the durability wavelength of 365
nm of hydrophilic nature using the mercury-vapor lamp of 17
mW/cm², and irradiating with the specimen cut down from each
coated steel sheet for 1 hour, the specimen was kept in the dark

place without an optical exposure. And after passing on the 1st, the opposite water contact angle was measured, what showed the value lower than durability fitness 0 and initial hydrophilicity for what was not different from initial hydrophilicity was made into x, and the durability of hydrophilic nature was evaluated.

[0028] The vertical x width =10x10 piece grid of 1-mm width was put into the film surface of the specimen cut down from film adhesion each coated steel sheet by the cutter, the exfoliation situation of the coat was investigated by the friction test using adhesive tape, that in which 0 and a coat exfoliated that from which coat exfoliation was not detected was made into x, and film adhesion was evaluated. The film surface was observed, after pressing gauze against the film surface of each specimen strongly and making it go and come back to it ten times. That to which powdering was bloomed or carried out and 0 and a coat exfoliated what change was not regarded as in the coat was made into x, and abrasion resistance was evaluated.

[0029] A 63 ** sunshine weather examination was presented with the weatherproof specimen, and the paint film state after 2000-hour progress was observed. That by which 0, the crack, and the white blush mark were observed in what abnormalities were not detected by the coat but was maintaining early transparency was made into x, and weatherability was evaluated.

[0030] Each paint of the test numbers 1-12 according to this invention was excellent in storage stability so that the results of an investigation of Table 1 might see. All presented the outstanding initial hydrophilicity of ten opposite water contact angles or less, and the durability, film adhesion, and weatherability of hydrophilic nature were also good so that the coated steel sheet obtained using each paint might also be seen in Table 2.

[0031] On the other hand, in the test number 13 whose water in a solvent and mass ratio of butyl cellosolve are 95:5, condensation arose at the time of paint preparation. In the test number 14 of 30:70, the mass ratio thickened at the time of paint

preparation, and, one month afterward, was gelling. In the test number 15 whose additions of an epoxy system silane coupling agent are five mass parts of titanium oxide, film adhesion was inferior. With the test number 16 of 70 mass parts, an addition did not show hydrophilic nature without UV irradiation, but weatherability was also inferior in it. In the test number 17 which uses an amino ** silane coupling agent, it gelled at the time of paint adjustment. As for by using the partially aromatic solvent which maintained the weight ratio of the water:organic solvent in the range of 10:90-60:40, the coated steel sheet which the paint excellent in storage stability was obtained and was obtained using this paint also shows excelling in hydrophilic nature, film adhesion, weatherability, etc. so that clearly from this contrast.

[0032]

表 1 : 各 塗 料 の 組 成 及 び 安 定 性

区分	試験番号	成膜法	混合溶媒(重量比)		TiO ₂	シランカップリング剤	安定性	
			水	ブチルセロソルブ			添加量(質量部)	調製直後
本発明例	1	1	70	30	40	なし	—	○ ○
	2	1	70	30	20	なし	—	○ ○
	3	1	50	50	40	なし	—	○ ○
	4	1	50	50	20	なし	—	○ ○
比較例	5	2	70	30	40	エポキシ系	30	○ ○
	6	2	70	30	20	エポキシ系	30	○ ○
	7	2	50	50	40	エポキシ系	30	○ ○
	8	2	50	50	20	エポキシ系	30	○ ○
	9	3	70	30	40	エポキシ系	30	○ ○
	10	3	70	30	20	エポキシ系	30	○ ○
	11	3	50	50	40	エポキシ系	30	○ ○
	12	3	50	50	20	エポキシ系	30	○ ○
	13	4	95	5	40	なし	—	凝聚
	14	4	30	70	40	なし	—	増粘 ゲル化
	15	5	70	30	40	エポキシ系	5	○ ○
	16	5	70	30	40	エポキシ系	70	○ ○
	17	6	70	30	40	アミノ系	80	ゲル化

[0033]

表2：各塗装鋼板の親水性及び塗膜性状

区分	試験番号	成膜法	焼成条件		対水接触角		塗膜性状	
			温度℃	時間分	初期値度	持続性	密着性	耐候性
本発明例	1	1	300	30	<10	○	○	○
	2	1	300	30	<10	○	○	○
	3	1	300	30	<10	○	○	○
	4	1	300	30	<10	○	○	○
	5	2	300	5	<10	○	○	○
	6	2	300	5	<10	○	○	○
	7	2	300	5	<10	○	○	○
	8	2	300	5	<10	○	○	○
	9	3	450	5	<10	○	○	○
	10	3	450	5	<10	○	○	○
	11	3	450	5	<10	○	○	○
	12	3	450	5	<10	○	○	○
比較例	15	5	300	5	<10	○	×	○
	16	5	300	5	65	○	○	×

[0034]

[Work example 2] the forming-membranes method 1 (example of this invention)

It rinsed and dried, after using the bright-annealing finishing material of the SUS304 stainless steel of 0.8 mm of board thickness for the paint negative and performing alkaline degreasing. a paint makes water and the partially aromatic solvent (water: butyl-cellosolve =70:30) of butyl cellosolve distribute boehmite -- boehmite -- it being considered as sol and, an anatase-type-titanium-oxide particle with a particle diameter of 7 nm -- distribution -- it adjusted by adding the epoxy system silane coupling agent (3-glycidoxypropyltrimetoxysilane) of 30 mass parts to

titanium oxide. The paint was applied to the stainless steel plate and the transparent photocatalyst distribution coat was formed by the heating calcination for 300 **x 5 minutes.

[0035] The forming-membranes method 2 (example of this invention)

the same stainless steel plate as the example 1 of membrane formation -- silica -- after forming a clear coat (the 1st layer) by applying sol and heating at 220 ** for 5 minutes, the transparent photocatalyst distribution coat was formed under the same conditions.

The example 3 (example of this invention) of membrane formation It changed to anatase-type-titanium-oxide particles, titanium tetraisopropoxide was dissolved in isopropanol, and the titanium oxide precursor which added diisopropanolamine was used. And the paint prepared on the same conditions as the example 1 of membrane formation was applied to the stainless steel plate, and the transparent photocatalyst distribution coat was formed by the calcination for 450 **x 5 minutes.

[0036] The example 4 (comparative example) of membrane formation The coat was formed like the example 1 of membrane formation except not adding a silane coupling agent.

The example 5 (comparative example) of membrane formation The coat was formed like the example 1 of membrane formation except calcinating at 180 **.

The example 6 (comparative example) of membrane formation the boehmite of the example 1 of membrane formation -- the silica which changed to sol and dissolved the tetraethoxysilane in ethanol -- the alumina sol which dissolved sol or aluminum isopropoxide in ethanol was used, and the transparent photocatalyst distribution coat which consists of silica, or formless alumina and titanium oxide was formed.

[0037] Each obtained coated steel sheet had the presentation shown in Table 3. The result of having estimated physical properties as working example 1 similarly is shown in Table 4. Each transparent photocatalyst distribution coat of the test numbers 1-6 according to this invention showed the ten or less

opposite water contact angle outstanding initial hydrophilicity, and its durability, film adhesion, and lightfastness of hydrophilic nature were also good so that the results of an investigation of Table 4 might see.

[0038] On the other hand, in the test number 7 using the paint which has not added the silane coupling agent, film adhesion was inferior. In the test number 8 with low calcination temperature, film adhesion was inferior similarly, and since there were many organic functional groups which remain in the coat, the crack and the white blush mark had arisen in the coat after a sunshine weather examination. In the test number 9 which used silica as the binder, hydrophilic nature was not shown without UV irradiation, but weatherability was also inferior. In the test number 10 which used formless alumina as the binder, hydrophilic nature was not shown without UV irradiation, but the hydrophilic nature after dark place storage also fell, and weatherability was also inferior.

[0039] It was checked by using the paint which added an appropriate amount of silane coupling agents that a transparent photocatalyst distribution coat with hydrophilic nature and film strength sufficient by short-time calcination is formed so that clearly from this contrast.

[0040]

表3：各塗装鋼板に形成した透明光触媒分散塗膜の組成

区分	試験番号	成膜法	クリア塗膜の有無	焼成条件		透明光触媒分散塗膜の組成				
				温度℃	時間分	シランカップリング剤	バインダ質量%	TiO ₂ 質量%	SiO ₂ 質量%	有機官能基質量%
本発明例	1	1	なし	300	80	無添加	ベーマイト γアルミナ 29 29	38	—	—
	2	1	なし	300	30	無添加	ベーマイト γアルミナ 39 39	19	—	—
	3	2	あり	300	5	添加	ベーマイト γアルミナ 29 29	38	3	1
	4	2	あり	300	5	添加	ベーマイト γアルミナ 39 39	19	2	1
	5	3	なし	450	5	添加	ベーマイト γアルミナ 29 29	38	3	1
	6	3	なし	450	5	添加	ベーマイト γアルミナ 39 39	19	2	1
比較例	7	4	なし	300	5	無添加	ベーマイト γアルミナ 30 30	40	—	—
	8	5	なし	180	5	添加	ベーマイト γアルミナ 27 27	35	3	8
	9	6	なし	300	5	添加	シリカ	35	3	10
	10	6	なし	300	5	添加	無定形アルミナ	54	36	3

[0041]

表4：各透明光触媒分散塗膜の物性

区分	試験番号	親水性		塗膜密着性	耐候性
		対水接触角、度 (初期親水性)	持続性		
本発明例	1	<10	○	○	○
	2	<10	○	○	○
	3	<10	○	○	○
	4	<10	○	○	○
	5	<10	○	○	○
	6	<10	○	○	○
比較例	7	<10	○	×	○
	8	89	○	×	×
	9	87	○	○	×
	10	88	×	○	×

[0042]

[Effect of the Invention] As explained above, the paint for

transparent photocatalyst distribution coat formation of this invention improves storage stability by using the partially aromatic solvent of water and an organic solvent, and it has controlled that a coat milks at the time of heat treatment. Therefore, the hydrophilic nature outstanding over the long period of time is maintained, it is highly transparent and the coated steel sheet with which the transparent transparent photocatalyst distribution coat excellent also in adhesion or weatherability was formed is manufactured.

- [Translation done.]